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ELECTRICAL CONDUCTANCE IN ORGANIC SOLIDS

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Abstract

This biannual progress report outlines the progress made during the sixth and seventh quarters of a two-year program to study the electrical characteristics of some organic solids. The work is divided along three general lines: a) the study of the transport of carriers injected into insulating (or poorly conducting) solids by an electron gun, b) a series of electrical measurements on a highly conducting ion radical salt of tetracyanoquinodimethan, and c) the study of carrier transport in some amorphous systems.

A cryostated electron gun system has been designed, and construction is nearing completion. This device should enable us to make transport measurements in a variety of insulating materials between 4° and 300° K.

Three techniques for determining the temperature coefficient of resistance of semi-metallic TCNQ salts have been investigated: (1) A. C. bridge methods for polycrystalline samples, (2) four-point-probe measurements on single crystals, and (3) microwave power loss in either polycrystalline or single crystal samples. Only the last appears promising, and further experiments with it are in progress.

The general direction and desired goals of this program are covered in the Technical Proposal submitted by the Principal Investigators on June 26, 1963. As of this date, no changes in program or intent are envisioned. It was proposed that certain research problems in three areas would be investigated: a) carrier transport in organic systems using electron injection, b) some physical measurements on tetracyanoquinodimethan ion radical salts, and c) determination of carrier mobilities and trapping in amorphous systems. Work has been pursued in each of three areas by the two principal investigators working individually and/or jointly.

Item a. "Study of Transport in Organic Crystals of Carriers Generated through Ionization by High-Energy Electrons"

Our preliminary experiments at room temperature established to our satisfaction that this technique is suitable for mobility measurements in organic systems. We have now proceeded to the design and construction of a cryostated apparatus that will enable us to make measurements from near liquid helium temperature to room temperature. Construction of this device in our shops is now nearly complete.

We were greatly assisted in design of the apparatus by R. W. Kopp of our laboratory Research Operation Services. A schematic diagram of the design is shown in Figure 1. The helium reservoir has a capacity of approximately 1 liter, and it is estimated the system will maintain temperature for the order of one week.

This apparatus also promises to be useful in other experiments aside from transport measurements, such as the measurement of electrical conductivities at low temperatures.

Item b. "On the Electrical and Magnetic Properties of TCNQ Ion-Radical Salts"

During the past contract period we have spent considerable time in measuring the electrical conductivity of one of the anion-radical salts of 7,7,8,8-tetracyanoquinodimethan (TCNQ). This salt, quinolinium$^+$ $(TCNQ_2)^-$, has been described as a semi-metal[1] because it exhibits a temperature-independent paramagnetic static susceptibility[1], a temperature-independent electron spin resonance absorption[2], and, over a limited temperature range, a temperature-independent electrical conductivity[3]. Several other TCNQ salts show similar behavior[3,4].

Conductivity measurements on quinolinium $(TCNQ_2)$ are difficult experimentally because the material is available only in the form of very fine needles (typical dimension 2 x 0.1 x 0.01 mm), which are therefore quite fragile. The most reliable conductivity results[3] were obtained using a four-point-probe technique, the value measured being $10^{+2}\,\Omega^{-1}\text{-cm}^{-1}$. The introduction of four contacts onto such a small needle inevitably results in appreciable strain, so that even the most modest temperature changes lead to fracture of the crystals. For this reason the temperature dependence

of conductivity could be determined by the four-point-probe technique only over the range 0° - 25° C; no variation was observed[3].

On the other hand, the conductivities of polycrystalline samples of quinolinium $(TCNQ_2)$ are much lower, $4\Omega^{-1}cm^{-1}$, and exhibit an Arrhenius temperature dependence with an activation energy of 0.03 eV[3]. These higher resistances are evidently caused by crystal-crystal and crystal-electrode contacts, and are no measure of intrinsic crystal phenomena.

A knowledge of the temperature dependence of conductivity over a wide temperature range would be of inestimable value in understanding the origin of the unusual electrical and magnetic properties of quinolinium $(TCNQ_2)$ and similar salts. We have attempted three experimental approaches.

The first involves A. C. measurements on polycrystalline samples as a function of frequency[4]. The assumption made in this technique is that at sufficiently high frequencies the high-resistance contacts are electrically shorted by their capacitance; the remaining resistance may then be attributed to the bulk resistance of the crystals themselves. This effect may be stated more explicitly by reference to figures 2 & 3. Attributing resistance R_s and capacitance C_s to the particles themselves, R_c and C_c to the contacts, then if $R_sC_s < R_sC_c$, the effective parallel resistance and capacitance measured by an A. C. bridge or Q-meter will be R_s and C_s for $WR_cC_c \gg 1$.

Measurements on polycrystalline samples of quinolinium $(TCNQ_2)$ were performed on two A. C. bridges from 1 kc to 100 kc and on a Q-meter from 100 kc to 50 mc. No change was observed either in effective parallel resistance or in effective parallel capacitance over this entire frequency range, indicating that even at 50 mc one is very far below the frequency of dispersion. On hindsight, this is probably an obvious result. Since the total d.c. resistance of the samples measured was only of the order of 100-1000 Ω, the contact capacitance would have to be very large indeed to make the dispersion frequency fall into an accessible range.

One curious phenomenon was observed in the course of these measurements: the polycrystalline samples of quinolinium $(TCNQ_2)$ had decidedly non-linear current-voltage characteristics. The

current generally varies as the square of the voltage for higher voltages, linearly at low applied voltage (see Figure 4). The current at given voltage is, of course, a function of the degree of packing of the polycrystalline sample. The transition from linear to square-law behavior appears to occur more nearly at the same current rather than at the same voltage in samples with different degrees of packing.

The second approach to conductivity measurements was simply an attempt to extend the temperature range of the previous four-point-probe results as far as possible. Contacts were made to the small needles by touching them with 0.002" copper wires wetted with conducting Ag paint. The crystal was supported by the four copper wires themselves, which had a length of about 1" and were soldered to a rigid base. The success/failure ratio in constructing these units without breaking the needle was about 1/3.

Four specimens were finally tested. All showed extremely large contact resistances; the d.c. resistance between any pair of contacts was generally of the order of 100Ω, whereas the four-probe resistance of all four specimens was 1Ω or less. Of the four specimens, one fractured immediately on cooling, another exhibited a rapidly rising resistance as the temperature was lowered to -100° C., then fractured upon warming between the voltage probes.

The two remaining specimens gave reproducible, reversible results between +25° and -100° C. However, the results were contradictory. In one crystal the four-probe resistance was independent of temperature over this entire range, whereas the two-probe resistance increased by a factor of about 50% at -100° C. In the other crystal, both the four-probe and two-probe resistance was higher by a factor of about 2 at -100° C than at +25° C. The most likely explanation is that the latter crystal contained some gross defect not present in the former. Both these crystals also fractured when an attempt was made to reduce their temperature to -150° C.

The four-probe measurements have been discontinued because they are too unprofitable for the effort expended. Our best result, based on one specimen only, indicates the conductivity to be independent of temperature between 25° and -100° C to an estimated error of 10%. This result, if true, is very surprising, for normal metals would exhibit almost a two-fold change in resistance over this range. The result is therefore suspect from both experimental and theoretical viewpoint.

A third experimental technique for conductivity-temperature measurements which we have investigated involves the determination of microwave power loss. We have observed such a phenomenon in the course of electron spin resonance studies of quinolinium $(TCNQ_2)$, the effect exhibiting itself by a decrease in Q of the ESR cavity upon insertion of a sample of the compound. A decrease in Q of about a factor of two was found for a 1 mg sample, and the change in Q^{-1} was proportional to sample size, as expected. The change in Q appeared to be independent of temperature down to -170° C, again indicating a temperature-independent conductivity.

An ESR cavity in its normal resonance mode is rather unsuitable for conduction loss measurements, however, since in this mode the sample is located at a maximum of the H field but at, or close to, a zero of the E field. Hence the loss is very sensitive to the exact sample positioning. We therefore intend to design and construct a special cavity into which a sample at controlled temperature can be inserted near a maximum in E.

Using the microwave loss technique it will not be possible to determine the absolute magnitude of the resistance, but it should be possible to determine relative magnitudes, and therefore the temperature dependence, rather easily.

References

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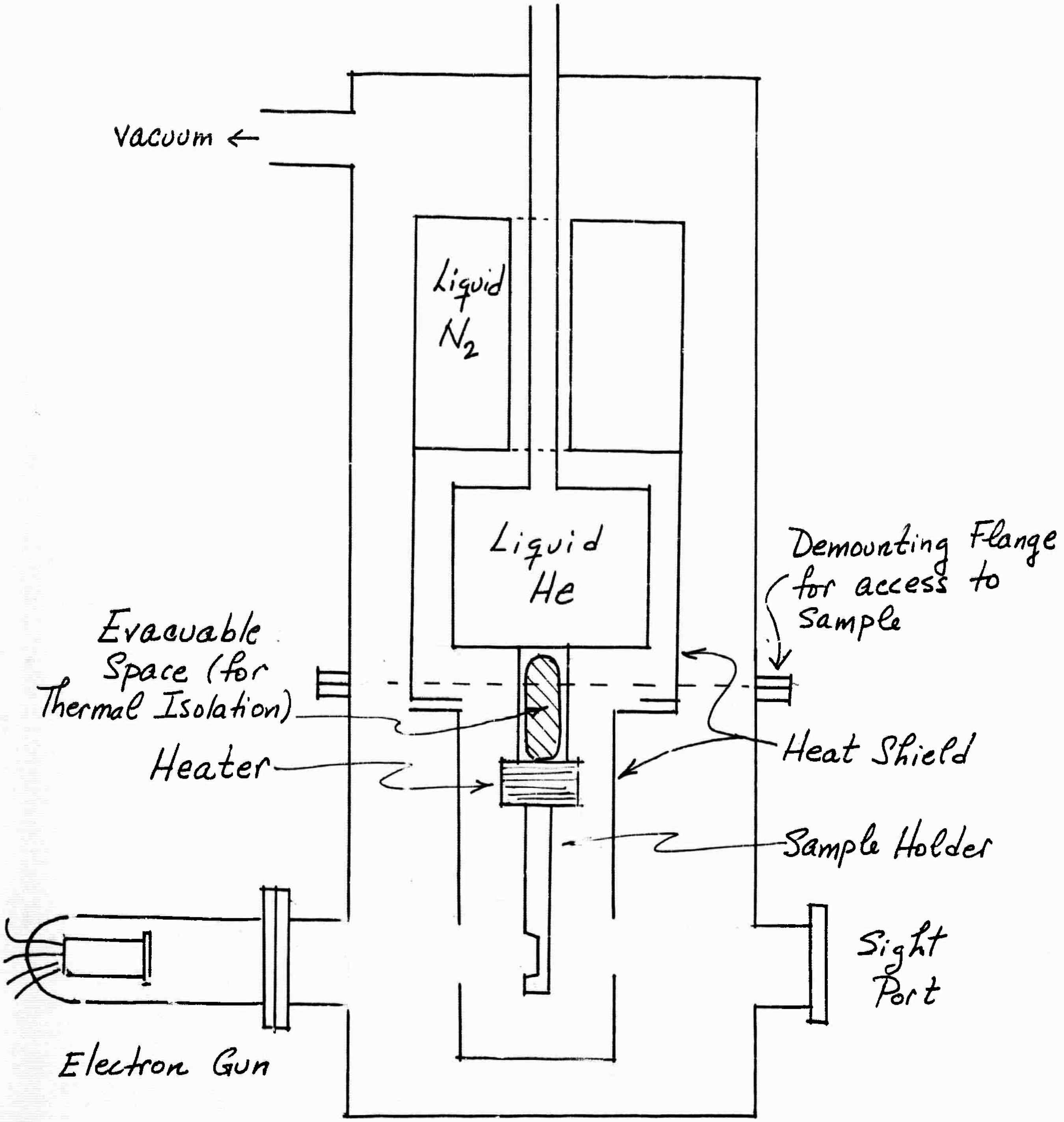


Figure 1. Schematic of cryostated electron gun design.

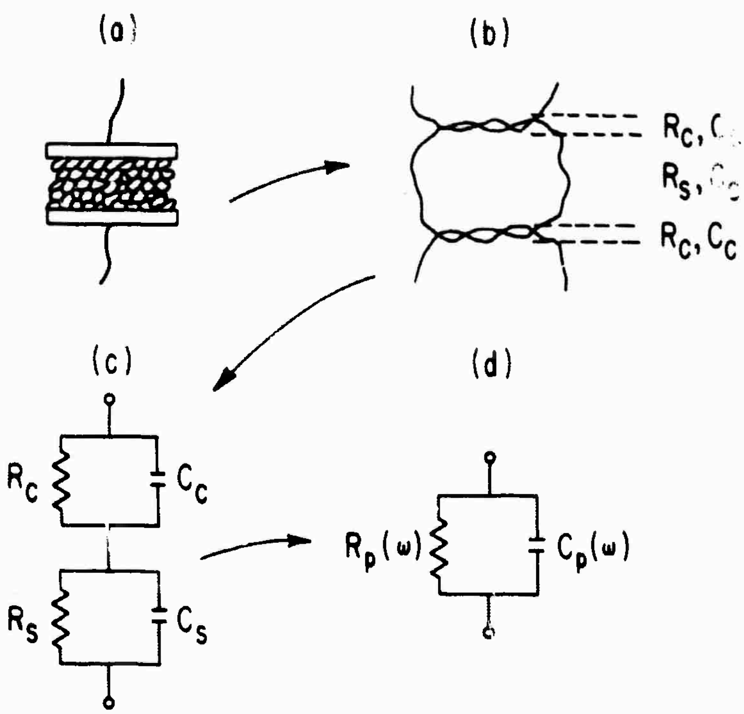
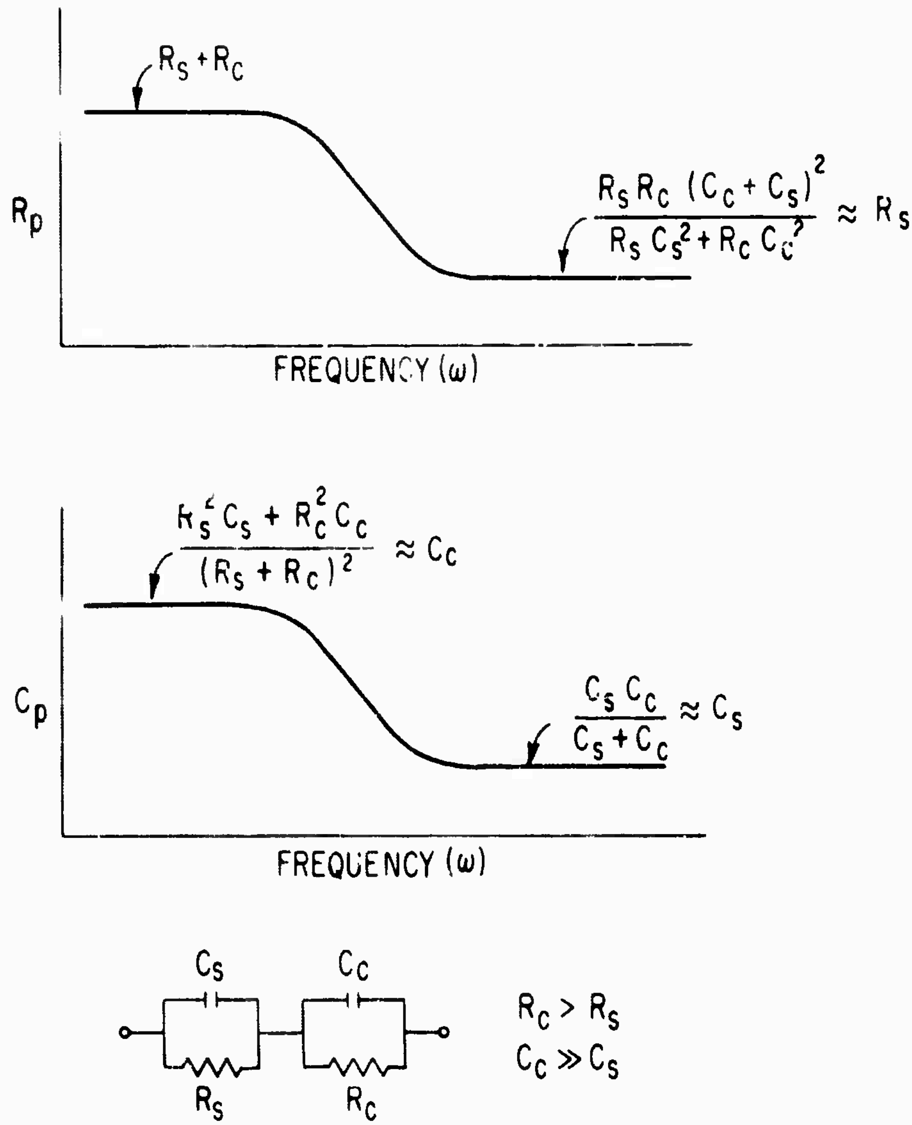


Figure 2



$R_s + R_c$
R_p
$\frac{R_s R_c (C_c + C_s)^2}{R_s C_s^2 + R_c C_c^2} \approx R_s$
FREQUENCY (ω)
$\frac{R_s^2 C_s + R_c^2 C_c}{(R_s + R_c)^2} \approx C_c$
C_p
$\frac{C_s C_c}{C_s + C_c} \approx C_s$
FREQUENCY (ω)
C_s
C_c
R_s
R_c
$R_c > R_s$
$C_c \gg C_s$

Fig. 3

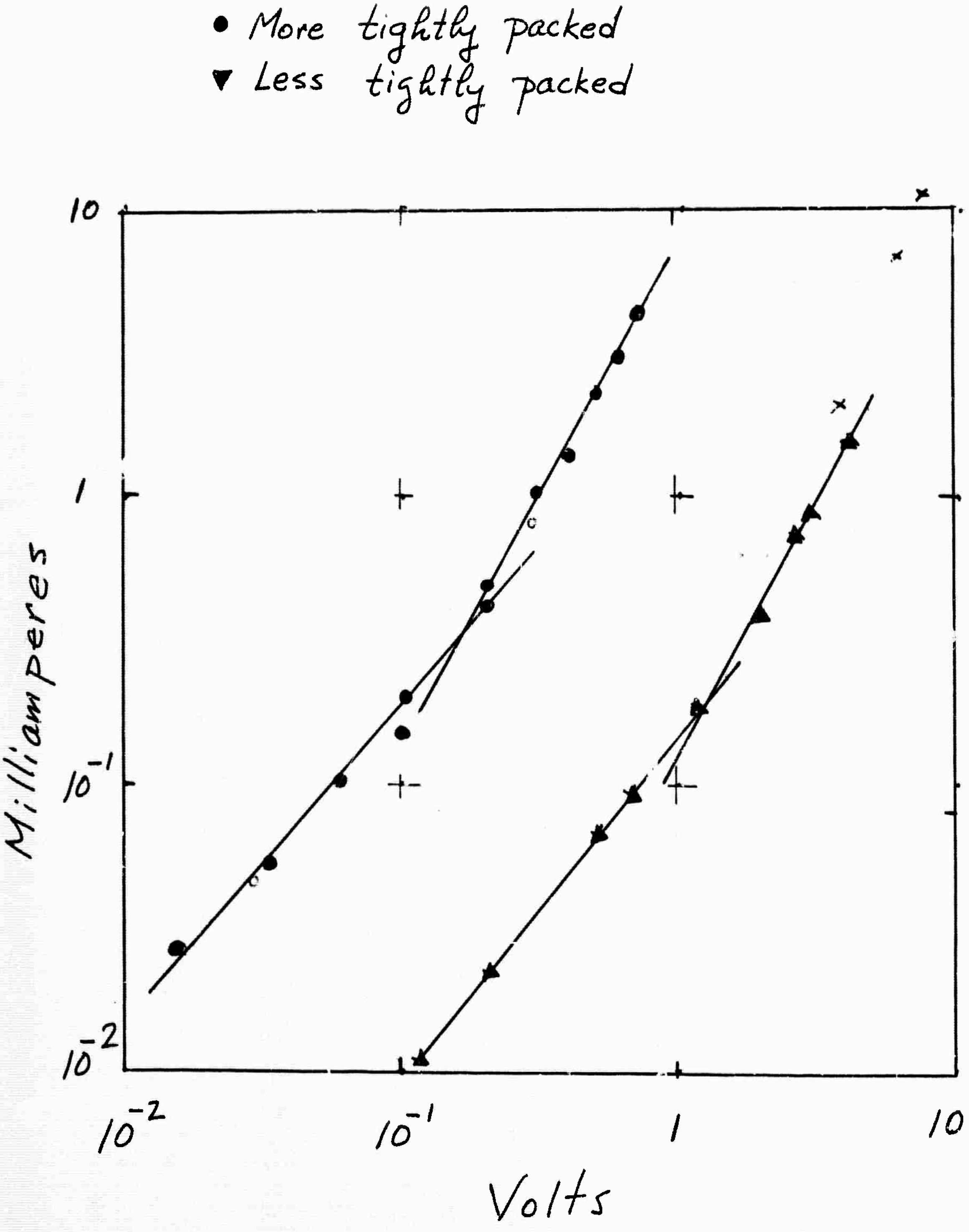


Figure 4. Current-voltage characteristics of polycrystalline samples of quinolinium$^{+}(TCNQ_2)^{-}$. T = 300°K, electrode spacing = 1.5 mm.